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(54) LAMINATED BODY HAVING ELECTRON CONDUCTOR LAYER AND ION CONDUCTOR LAYER AND ITS MANUFACTURE

(57)Abstract:
PURPOSE: To extend the surface areas of both layers, in a laminated body having an electron conductor layer and an ion conductor layer at least one of which consists of an inorganic oxide, to enhance reaction efficiency, and smoothly move electrons and ions in an electrode reaction.
CONSTITUTION: In a laminated body having an electron conductor layer and an ion conductor layer at least one of which consists of an inorganic oxide, the critical surfaces of both the layers irregularly make contact to each other to increase the areas of the critical surfaces.

* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1]A layered product, wherein an interface of said both layers touches rugged form in a layered product which has an electronic conductor layer which at least one side becomes from an inorganic oxide, and an ion conductor layer.
[Claim 2]In a layered product which has an electronic conductor layer which at least one side becomes from an inorganic oxide, and an ion conductor layer, A layered product, wherein a mixed layer of both conductors that electron conductive particles distributed uniformly in an ion conductor layer formed by the Sol-Gel method exists in an interface of said both layers in which one of these has unevenness at least.
[Claim 3]A manufacturing method of the layered product according to claim 1 making a conductor layer of another side form by the Sol-Gel method on one [which has unevenness] layer of an electronic conductor layer or an ion conductor layer.
[Claim 4]A manufacturing method of the layered product according to claim 2 using coating liquid for ion conductor stratification which distributed electron conductive particles uniformly in it for an interface of an electronic conductor layer by which unevenness is formed at least in one of these, and an ion conductor layer, and making said mixture layer form by the Sol-Gel method.
[Claim 5]A solid state battery, wherein an interface of a positive active material layer and a solid electrolysis material layer touches rugged form in a solid state battery which has a positive active material layer, a solid electrolyte layer, and a negative electrode active material layer.
[Claim 6]A solid state battery, wherein a positive active material layer where one of these has unevenness at least in a solid state battery which has a positive active material layer, a solid electrolyte layer, and a negative electrode active material layer, and a mixture layer which positive-active-material particles distributed uniformly all over a solid electrolyte layer to an interface of a solid electrolyte layer exist.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the layered product which has an electronic conductor layer which consists of inorganic oxides, and an ion conductor layer, and its manufacturing method.
[0002]
[Description of the Prior Art]Although the element which used the electrochemical reaction of the electrode like a cell or an electrochromic device is conventionally used by the solution system, by these days, solidification of the element is considered in consideration of combination, space development, etc. with various electric appliances and electronic equipment. In the interface of the electrode active material and solid electrolyte of a solid state component, the characteristic that it is [the contact state of both layers] very important it in order that movement of an electron and ion may start with an oxidation-reduction reaction, and it is good only by pasting an electrode active material and a solid electrolyte together is hard to be obtained. In order to start the chemical reaction which is the characteristic of an element by an interface, for mentioning reaction efficiency, it should just enlarge surface area of the interface. That is, the interface of an electronic conduction layer and an ionic conduction layer is high surface area, and the element which has the good characteristic needs to be excellent in an electronic transition and ion migration reactivity. In the interface of an electronic conduction layer and an ionic conduction layer, in an inorganic material comrade's laminated constitution, since material is hard and it is weak, restrictions are large and realization is difficult. This invention solved these problems and it aimed at obtaining this layered product that has a high surface area interface. In order to raise the electronic transition and ion migration reactivity in an interface, providing the mixed layer of an electrode active material and a solid electrolyte in the interface of both layers was proposed, and effect was taken. That is, it excels in pliability in a solid electrolyte layer, the layer which used manganese dioxide with large service capacity for the active material layer for the solid polymer electrolyte which can be cast again, and distributed active material powder in the solid electrolyte is provided in both interface, and examination is made. Generally ionic conductivity of a polymer electrolyte is low. On the other hand, it is NASICON ($NalZr_2SixPmO_{12}$ or NalZrnSixPmOw: among a before type) as a solid electrolyte with high ionic conductivity. l=1+x,m=3-x,n=2-3/x,w=12-2x/3 -- expressing -- lithium conductivity glass, such as LISICON (presentation which changed Nay Cong's Na to Li), is known. These inorganic oxides are obtained by calcinating the solid powder which is generally a raw material at an elevated temperature, and, generally a limit is for a sintered compact to mix atomization and a sintered compact comrade homogenously.
[0003]
[Objects of the Invention]In the layered product which has an electronic conductor layer which at least one side becomes from an inorganic oxide, and an ion conductor layer, the surface area of this invention of the interface of said both layers is large, and an object of this invention is to provide the layered product which was excellent in this interface at an electronic transition and ion migration nature.
[0004]
[Elements of the Invention]In a layered product for which one of the layered products of this invention has an electronic conductor layer which at least one side becomes from an inorganic oxide, and an ion conductor layer, It is characterized by an interface of both layers touching rugged form, and, as for the two, said electronic conductor layer and a mixed layer of said electronic conductor and an ion conductor which at least one side of an ion conductor layer is rugged form, and were formed in an interface of these both layers by the Sol-Gel method exist. Hereafter, it explains concretely. An electronic conductor layer which consists of an inorganic

oxide used by this invention comprises vanadium pentoxide (V_2O_5), manganese dioxide (MnO_2), etc., for example. An ion conductor layer which consists of an inorganic oxide used by this invention comprises beta-alumina generally known as a solid electrolyte, NASICON, and LISICON. After producing a sintered compact of an electronic conductor or an ion conductor, formation of unevenness to both sides or one side of these electronic conductor layers and ion conductor layers may cut mechanically, and may pattern using a lithography technology, for example. Or these sintered compacts may be produced by the Sol-Gel method, and it may patternize by mold omission at the time of gelling. A layered product which said both conductor layer joined with sufficient adhesion can be obtained by forming other conductor layers by the Sol-Gel method on one conductor layer of an electronic conductor layer which formed unevenness beforehand by above methods, or an ion conductor layer. In using an electronic conductor layer and an ion conductor layer by which unevenness is formed in at least one conductor layer by above methods, A layered product which said both conductor layer joined with sufficient adhesion can be obtained by making a mixture layer of said electronic conductor and an ion conductor form in an interface of both conductor layer by the Sol-Gel method. Formation of said mixture layer by the Sol-Gel method, For example, coating liquid which can form an ion conductor layer by the Sol-Gel method is created, On an electronic conductor layer by which unevenness is formed in at least one conductor layer, and/or an ion conductor layer, the dry afterbaking join of what distributed inorganic electron conductivity particles in this coating solution can be applied and carried out, and it can be formed. The Sol-Gel method is a manufacturing method of an inorganic oxide which completes organic metal compounds, such as a metal alkoxide, by a solution system hydrolysis and by carrying out a polycondensation, growing up a metal-oxygen-metallic bond and sintering it eventually. A manufacturing method of an inorganic oxide by the Sol-Gel method specifically applies on a substrate a solution containing an organic metal compound, and performs a dry afterbaking join. As an organic metal compound used, alkoxides, acetate compounds, etc. which constitute an inorganic oxide, such as a metaled methoxide, ethoxide, propoxide, and butoxide, are raised. Mineral salt of a nitrate, an oxalate, a perchlorate, etc. may be sufficient. Since it is necessary to advance hydrolysis and a polycondensation reaction for producing an inorganic oxide from these compounds, in a coating solution, addition of water is needed. An addition becomes uneven [membraneous quality obtained in order that a reaction may progress quickly, if too large, although it changes with systems] easily, and control of reaction velocity is difficult for it. Even if there are too few additions of water, control of a reaction is difficult, and there is optimum dose. If a hydrolysis catalyst is added, control of reaction velocity and a reaction gestalt can be performed. Acid and a base general as a catalyst are used. In order to dissolve these raw materials uniformly, a solvent is used, but as for this, that in which the above-mentioned material does not precipitate, i.e., a thing excellent in compatibility, is desirable. although solution concentration is based also on a coating method -- a case of a spin coat method -- solution viscosity -- several cP-about ten -- it is good to adjust so that it may be set to cP. A chelating agent etc. which stabilize a metal alkoxide other than these may be added. According to the Sol-Gel method, an inorganic oxide can be obtained at low temperature from the usual production temperature irrespective of gestalten, such as particles, a film, and bulk. In production of particles, a path of particles can be made small, and since a starting material is a solution when mixing is required, homogeneity can be distributed. In film production, in order to produce from a solution by spreading, a film [that it is uniform and large area] can be obtained, and it excels in adhesion with a substrate. It can produce comparatively easily on a substrate of any shape. If these features are used, an electronic conduction layer and an ionic conduction layer can obtain a layered product which touches with adhesion sufficient to rugged form by the Sol-Gel method. A layered product by which electron conductive particles were uniformly distributed by interface of both layers in an ion conductor was able to be stuck to rugged form, and was able to be produced. A layered product of this invention can be used for a solid secondary battery, an electrochromic element, a sensor, etc. as it is. For example, as positive active material, LISICON is used for a solid electrolyte for vanadium pentoxide or manganese dioxide, and if lithium is used as negative electrode active material, a solid secondary battery is producible. An electrochromic element is producible, if tungstic oxide is used for a working pole, a transparent electrode is used for a counter electrode and a solid electrolyte is inserted. An active material and a solid electrolyte interface which consist of inorganic oxides are improved by existence of both mixed layer, and these solid state components can perform an outstanding redox reaction.

[0005]

[Example]

The powder of manganese dioxide and acetylene black which is conducting agents was mixed as an example 1

electronic-conduction layer (anode), it pressed, tabular was processed, and unevenness 100 micrometers in width and 5 micrometers in depth was formed in the surface in a 100-micrometer pitch. Besides, an ionic conduction layer is produced from the coating liquid which dissolved $Zr(OC_3H_7)_4$, $Si(OC_2H_5)_4$, $PO(OC_4H_9)_3$, and the alkoxide and water of Li (OC_4H_9) into 2-methoxyethanol, After 120 ** dried for 5 minutes, it sintered at 600 **. This spreading - a sintering process were repeated, 10 micrometers of ionic conduction layers of LISICON were produced, and the layered product of an electronic conductor and an ion conductor was produced. [Drawing 2 (a)] .Next, 1000A of metal lithium (negative electrode) was vapor-deposited to the solid electrolyte side of the obtained layered product, metal foil was stuck further by pressure, and the lithium cell was produced. [Drawing 2 (b)] .Even if the interfacial resistance of the anode by measurement of the frequency characteristic of impedance and a solid electrolyte repeated charge and discharge 50 times, change was hardly seen.

The manganese dioxide sintered compact which has unevenness on the surface like example 2 Example 1 is produced, Besides, the mixed layer of an electronic conductor and an ion conductor, A film is produced using the coating liquid which dissolved $Zr(OC_3H_7)_4$, $Si(OC_2H_5)_4$, $PO(OC_4H_9)_3$, and the alkoxide and water of Li (OC_4H_9) in the 2-methoxyethanol which distributed manganese dioxide powders, After 120 ** dried for 5 minutes, it sintered at 600 **. This spreading - a sintering process were repeated and a 2000-A mixed layer was produced. Then, on this, 10 micrometers of ionic conduction layers of LISICON were produced from the solution of the presentation excluding manganese dioxide from the above-mentioned coating liquid, and the layered product of an electronic conductor and an ion conductor was produced. [Drawing 3 (a)] .Next, 1000A of metal lithium (negative electrode) was vapor-deposited to the solid electrolyte side of the obtained layered product, metal foil was stuck further by pressure, and the lithium cell was produced. [Drawing 3 (b)] .Even if the interfacial resistance of the anode by measurement of the frequency characteristic of impedance and a solid electrolyte repeated charge and discharge 50 times, change was hardly seen.

[0006]

[Effect]When the interface of an electronic conductor layer and an ion conductor layer touched rugged form, the surface area of the interface was able to be made to have been able to expand and reaction efficiency was able to be raised. Furthermore, the layered product with good movement of the electron in an electrode reaction and ion was obtained by providing the mixture of said both conductors in the interface of said both layers.

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TECHNICAL FIELD

[Field of the Invention]This invention relates to the layered product which has an electronic conductor layer which consists of inorganic oxides, and an ion conductor layer, and its manufacturing method.

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PRIOR ART

[Description of the Prior Art]Although the element which used the electrochemical reaction of the electrode like a cell or an electrochromic device is conventionally used by the solution system, by these days, solidification of the element is considered in consideration of combination, space development, etc. with various electric appliances and electronic equipment. In the interface of the electrode active material and solid electrolyte of a solid state component, the characteristic that it is [the contact state of both layers] very important it in order that movement of an electron and ion may start with an oxidation-reduction reaction, and it is good only by pasting an electrode active material and a solid electrolyte together is hard to be obtained. In order to start the chemical reaction which is the characteristic of an element by an interface, for mentioning reaction efficiency, it should just enlarge surface area of the interface. That is, the interface of an electronic conduction layer and an ionic conduction layer is high surface area, and the element which has the good characteristic needs to be excellent in an electronic transition and ion migration reactivity. In the interface of an electronic conduction layer and an ionic conduction layer, in an inorganic material comrade's laminated constitution, since material is hard and it is weak, restrictions are large and realization is difficult. This invention solved these problems and it aimed at obtaining this layered product that has a high surface area interface. In order to raise the electronic transition and ion migration reactivity in an interface, providing the mixed layer of an electrode active material and a solid electrolyte in the interface of both layers was proposed, and effect was taken. That is, it excels in pliability in a solid electrolyte layer, the layer which used manganese dioxide with large service capacity for the active material layer for the solid polymer electrolyte which can be cast again, and distributed active material powder in the solid electrolyte is provided in both interface, and examination is made. Generally ionic conductivity of a polymer electrolyte is low. On the other hand, it is NASICON ($NalZr_2SixPmO_{12}$ or NalZrnSixPmOw: among a before type) as a solid electrolyte with high ionic conductivity. l=1+x,m=3-x,n=2-3/x,w=12-2x/3 -- expressing -- lithium conductivity glass, such as LISICON (presentation which changed Nay Cong's Na to Li), is known. These inorganic oxides are obtained by calcinating the solid powder which is generally a raw material at an elevated temperature, and, generally a limit is for a sintered compact to mix atomization and a sintered compact comrade homogenously.

[0003]

[Objects of the Invention]In the layered product which has an electronic conductor layer which at least one side becomes from an inorganic oxide, and an ion conductor layer, the surface area of this invention of the interface of said both layers is large, and an object of this invention is to provide the layered product which was excellent in this interface at an electronic transition and ion migration nature.

[0004]

[Elements of the Invention]In a layered product for which one of the layered products of this invention has an electronic conductor layer which at least one side becomes from an inorganic oxide, and an ion conductor layer, It is characterized by an interface of both layers touching rugged form, and, as for the two, said electronic conductor layer and a mixed layer of said electronic conductor and an ion conductor which at least one side of an ion conductor layer is rugged form, and were formed in an interface of these both layers by the Sol-Gel method exist. Hereafter, it explains concretely. An electronic conductor layer which consists of an inorganic oxide used by this invention comprises vanadium pentoxide (V_2O_5), manganese dioxide (MnO_2), etc., for example.

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EFFECT OF THE INVENTION

[Effect]When the interface of an electronic conductor layer and an ion conductor layer touched rugged form, the surface area of the interface was able to be made to have been able to expand and reaction efficiency was able to be raised. Furthermore, the layered product with good movement of the electron in an electrode reaction and ion was obtained by providing the mixture of said both conductors in the interface of said both layers.

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EXAMPLE

[Example]
The powder of manganese dioxide and acetylene black which is conducting agents was mixed as an example 1 electronic-conduction layer (anode), it pressed, tabular was processed, and unevenness 100 micrometers in width and 5 micrometers in depth was formed in the surface in a 100-micrometer pitch. Besides, an ionic conduction layer is produced from the coating liquid which dissolved $Zr(OC_3H_7)_4$, $Si(OC_2H_5)_4$, $PO(OC_4H_9)_3$, and the alkoxide and water of Li (OC_4H_9) into 2-methoxyethanol, After 120 ** dried for 5 minutes, it sintered at 600 **. This spreading - a sintering process were repeated, 10 micrometers of ionic conduction layers of LISICON were produced, and the layered product of an electronic conductor and an ion conductor was produced. [Drawing 2 (a)] .Next, 1000A of metal lithium (negative electrode) was vapor-deposited to the solid electrolyte side of the obtained layered product, metal foil was stuck further by pressure, and the lithium cell was produced. [Drawing 2 (b)] .Even if the interfacial resistance of the anode by measurement of the frequency characteristic of impedance and a solid electrolyte repeated charge and discharge 50 times, change was hardly seen.
The manganese dioxide sintered compact which has unevenness on the surface like example 2 Example 1 is produced, Besides, the mixed layer of an electronic conductor and an ion conductor, A film is produced using the coating liquid which dissolved $Zr(OC_3H_7)_4$, $Si(OC_2H_5)_4$, $PO(OC_4H_9)_3$, and the alkoxide and water of Li (OC_4H_9) in the 2-methoxyethanol which distributed manganese dioxide powders, After 120 ** dried for 5 minutes, it sintered at 600 **. This spreading - a sintering process were repeated and a 2000-A mixed layer was produced. Then, on this, 10 micrometers of ionic conduction layers of LISICON were produced from the solution of the presentation excluding manganese dioxide from the above-mentioned coating liquid, and the layered product of an electronic conductor and an ion conductor was produced. [Drawing 3 (a)] .Next, 1000A of metal lithium (negative electrode) was vapor-deposited to the solid electrolyte side of the obtained layered product, metal foil was stuck further by pressure, and the lithium cell was produced. [Drawing 3 (b)] .Even if the interfacial resistance of the anode by measurement of the frequency characteristic of impedance and a solid electrolyte repeated charge and discharge 50 times, change was hardly seen.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1](a) shows the sectional view of the layered product which consists of an electronic conduction layer which has unevenness, and an ionic conduction layer.
(b) shows the sectional view of the layered product which provided the mixed layer in the interface of an ionic conduction layer and the electronic conduction layer which has unevenness.
[Drawing 2]MnO_2 and an ionic conduction layer comprise LISICON, and, as for (a), an electronic conduction layer shows the sectional view of a layered product whose interface of both layers is rugged form.
(b) shows the sectional view of the layered product which formed a vacuum evaporation Li layer and Li foil on the LISICON layer of the above (a), respectively.
[Drawing 3](a) shows the sectional view of the layered product which becomes an interface of a LISICON layer and the MnO_2 layer which provided unevenness from LISICON and MnO_2.
(b) shows the sectional view of the layered product which formed a vacuum evaporation Li layer and Li foil on the LISICON layer of the above (a), respectively.
[Description of Notations]
1 Electronic conduction layer
2 Mixed layer
3 Ionic conduction layer
4 Vacuum evaporation Li layer
5 Li foil

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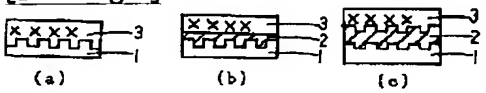
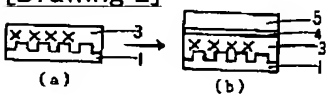
DRAWINGS

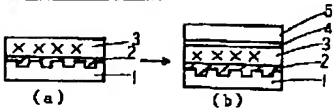
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)**公開特許公報（Ａ）**　(11)特許出願公開番号

特開平5－109429

(43)公開日　平成5年(1993)4月30日

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H01M 10/38		8939－4K		
G02F 1/15	507	8807－2K		
H01B 1/06		7244－5G	A	
H01M 4/02		8939－4K	A	

審査請求　未請求　請求項の数6（全　4　頁）

(21)出願番号　特願平3－293677

(22)出願日　平成3年(1991)10月14日

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(74)代理人　弁理士　友松　英爾

(54)【発明の名称】　電子伝導体層とイオン伝導体層とを有する積層体およびその製造法

(57)【要約】
【目的】　本発明は、少なくとも一方が無機酸化物からなる電子伝導体層とイオン伝導体層とを有する積層体において、前記両層の表面積が広く反応効率が高く、電極反応における電子やイオンの移動が良好な積層体の提供を目的とする。
【構成】　少なくとも一方が無機酸化物からなる電子伝導体層とイオン伝導体層とを有する積層体において、前記両層の界面が凹凸状に接触し、その界面の面積が拡大していることを特徴とする積層体。

1

【特許請求の範囲】

【請求項１】　少なくとも一方が無機酸化物からなる電子伝導体層とイオン伝導体層とを有する積層体において、前記両層の界面が凹凸状に接触していることを特徴とする積層体。

【請求項２】　少なくとも一方が無機酸化物からなる電子伝導体層とイオン伝導体層とを有する積層体において、少なくともその一方が凹凸を有する前記両層の界面に、Ｓｏｌ－Ｇｅｌ法で形成されたイオン伝導体層中に電子伝導性粒子が均一に分散した両伝導体の混合層が存在することを特徴とする積層体。

【請求項３】　凹凸を有する電子伝導体層あるいはイオン伝導体層の一方の層上に、Ｓｏｌ－Ｇｅｌ法により他方の伝導体層を形成させることを特徴とする請求項１記載の積層体の製造法。

【請求項４】　少なくともその一方に凹凸が形成されている電子伝導体層とイオン伝導体層の界面に、電子伝導性粒子をその中に均一に分散させたイオン伝導体層形成用の塗布液を使用し、Ｓｏｌ－Ｇｅｌ法により前記混合物層を形成させることを特徴とする請求項２記載の積層体の製造法。

【請求項５】　正極活物質層、固体電解質層および負極活物質層を有する固体電池において、正極活物質層と固体電解物質層の界面が凹凸状に接触していることを特徴とする固体電池。

【請求項６】　正極活物質層、固体電解質層および負極活物質層を有する固体電池において、少なくともその一方が凹凸を有する正極活物質層と固体電解質層の界面に、固体電解質層中に正極活物質粒子が均一に分散した混合物層が存在することを特徴とする固体電池。

【発明の詳細な説明】

【０００１】

【技術分野】本発明は、無機酸化物からなる電子伝導体層とイオン伝導体層とを有する積層体およびその製造法に関する。

【０００２】

【従来技術】電池やエレクトロクロミックデバイスのように電極の電気化学反応を利用した素子は従来溶液系で利用されているが、最近では各種電気機器、電子機器との組合せや宇宙開発等を考慮して素子の固体化が検討されている。固体素子の電極活物質と固体電解質の界面では、酸化還元反応と共に電子やイオンの移動がおこるため両層の接触状態が大変重要であり、電極活物質と固体電解質とを張り合わせるだけでは良好な特性が得られにくい。また、素子の特性である化学反応は界面でおこるため反応効率を挙げるには界面の表面積を大きくしてあげれば良い。すなわち、良好な特性を有する素子は電子伝導層とイオン伝導層の界面が高表面積でかつ電子移動及びイオン移動反応性に優れている必要がある。電子伝導層とイオン伝導層の界面においては、無機材料同志の

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積層構成では材料が固くて脆いため制約が大きく実現が難しい。本発明はこれらの問題を解決し、高表面積界面を有する該積層体を得ることを目的とした。界面における電子移動及びイオン移動反応性を向上させるため、両層の界面に電極活物質と固体電解質の混合層を設けることが提案され、効果が示された。すなわち、固体電解質層に柔軟性に優れ、キャスティングが可能な高分子固体電解質を、また、活物質層に放電容量の大きい二酸化マンガンを用いて固体電解質中に活物質粉末を分散させた層を両者の界面に設けて検討がなされている。高分子電解質は一般にイオン伝導度が低い。一方、イオン伝導度が高い固体電解質として、ＮＡＳＩＣＯＮ（$Na_1Zr_2Si_xPm_{12}$ またはNa_1ZrnSi_xPmOw：前式中、ｌ＝１＋ｘ，ｍ＝３－ｘ，ｎ＝２－３／ｘ，ｗ＝１２－２ｘ／３を表わす）やＬＩＳＩＣＯＮ（ナイコンのＮａがＬｉに変った組成）等のリチウム伝導性ガラスが知られている。これらの無機酸化物は一般に原料である固体粉末を高温で焼成して得られ、一般的に焼結体は微粒子化や焼結体同志を均一混合するのに限界がある。

【０００３】

【目的】本発明は、少なくとも一方が無機酸化物からなる電子伝導体層とイオン伝導体層とを有する積層体において、前記両層の界面の表面積が広く、該界面で電子移動及びイオン移動性に優れた積層体を提供することを目的とする。

【０００４】

【構成】本発明の積層体の１つは、少なくとも一方が無機酸化物からなる電子伝導体層とイオン伝導体層とを有する積層体において、両層の界面が凹凸状に接触していることを特徴とするものであり、その２つは、前記電子伝導体層と、イオン伝導体層の少なくとも一方が凹凸状であり、かつ該両層の界面にＳｏｌ－Ｇｅｌ法で形成された前記電子伝導体とイオン伝導体の混合層が存在することを特徴とする。以下、具体的に説明する。本発明で用いられる無機酸化物からなる電子伝導体層は、例えば五酸化バナジウム（V_2O_5）や二酸化マンガン（MnO_2）などから構成される。本発明で用いられる無機酸化物からなるイオン伝導体層は、一般に固体電解質として知られているβ－アルミナやＮＡＳＩＣＯＮ、ＬＩＳＩＣＯＮから構成される。これらの電子伝導体層とイオン伝導体層の双方あるいは一方への凹凸の形成は、例えば電子伝導体、またはイオン伝導体の焼結体を作製後、機械的に切削加工を行っても良いし、リソグラフィー技術を用いてパターニングを行っても良い。あるいは、これらの焼結体をＳｏｌ－Ｇｅｌ法により作製し、ゲル化の時点で型抜きによりパターン化しても良い。前記のような方法で凹凸をあらかじめ形成した電子伝導体層あるいはイオン伝導体層の一方の伝導体層上に、Ｓｏｌ－Ｇｅｌ法により他の伝導体層を形成することにより、前記両

伝導体層が密着性良く接合した積層体を得ることができる。また、前記のような方法により少なくとも一方の伝導体層に凹凸が形成されている電子伝導体層およびイオン伝導体層を使用する場合には、両伝導体層の界面に、Ｓｏｌ－Ｇｅｌ法により前記電子伝導体とイオン伝導体の混合物層を形成させることにより、前記両伝導体層が密着性良く接合した積層体を得ることができる。Ｓｏｌ－Ｇｅｌ法による前記混合物層の形成は、例えば、Ｓｏｌ－Ｇｅｌ法によってイオン伝導体層を形成することのできる塗布液を作成し、該塗布溶液中に無機電子伝導性粒子を分散させたものを、少なくとも一方の伝導体層に凹凸が形成されている電子伝導体層および／またはイオン伝導体層上に塗布し、乾燥後焼結して形成することができる。Ｓｏｌ－Ｇｅｌ法とは金属アルコキシド等の金属有機化合物を溶液系で加水分解、重縮合させて金属－酸素－金属結合を成長させ、最終的に焼結することにより完成させる無機酸化物の作製方法である。Ｓｏｌ－Ｇｅｌ法による無機酸化物の作製方法は、具体的には基板上に金属有機化合物を含む溶液を塗布し、乾燥後焼結を行う。用いられる金属有機化合物としては、無機酸化物を構成する金属のメトキシド、エトキシド、プロポキシド、ブトキシド等のアルコキシドやアセテート化合物等があげられる。硝酸塩、しゅう酸塩、過塩素酸塩、等の無機塩でも良い。これら化合物から無機酸化物を作製するには加水分解および重縮合反応を進める必要があるため塗布溶液中には水の添加が必要となる。添加量は系により異なるが多すぎると反応が速く進むため得られる膜質が不均一となり易く、また反応速度の制御が難しい。水の添加量が少なすぎても反応のコントロールが難しく、適量がある。さらに、加水分解触媒を添加すると反応速度及び、反応形態の制御ができる。触媒としては一般の酸および塩基が用いられる。これらの原料を均一に溶解させるため溶媒を用いるが、これは上記材料が沈殿しないもの、すなわち相溶性に優れたものが望ましい。溶液濃度は塗布方法にもよるが、スピンコート法の場合溶液粘度が数ｃＰ～十数ｃＰとなるように調整すると良い。これらの他に金属アルコキシドを安定化するキレート剤等を添加しても良い。Ｓｏｌ－Ｇｅｌ法によれば、粒子、膜、バルクなどの形態にかかわらず、通常の作製温度より低温で無機酸化物を得ることができる。粒子の作製においては粒子の径を小さくすることができ、また混合が必要なときは出発物質が溶液であるため均一に分散させることができる。製膜においては、塗布によって溶液から作製するため、均一で大面積な膜を得ることができ、基板との密着性に優れる。またどんな形状の基板上にも比較的容易に作製することができる。これらの特徴を利用すると、Ｓｏｌ－Ｇｅｌ法により、電子伝導層とイオン伝導層が凹凸状に密着良く接触している積層体を得ることができる。また、両層の界面にイオン伝導体中に電子伝導性粒子が均一に分散された積層体を凹凸状に密着させて作製することができた。本発明の積層体はそのまま固体二次電池やエレクトロクロミック素子、センサーなどに使用することができる。例えば正極活物質として五酸化バナジウムや二酸化マンガンを、固体電解質にＬＩＳＩＣＯＮを用い、負極活物質としてリチウムを使用すれば固体二次電池を作製できる。また、作用極に酸化タングステン、対極に透明電極を用いて固体電解質をはさめばエレクトロクロミック素子を作製できる。これらの固体素子は無機酸化物からなる活物質と固体電解質界面が両者の混合層の存在により改善されており、優れたレドックス反応を行うことができる。

【０００５】

【実施例】

実施例１

電子伝導層（正極）として二酸化マンガンと導電剤であるアセチレンブラックの粉末を混合し、プレスして板状に加工し、表面に巾１００μｍ、深さ５μｍの凹凸を１００μｍピッチで形成した。この上にイオン伝導層を２－メトキシエタノール中に$Zr(OC_3H_7)_4$，$Si(OC_2H_5)_4$，$PO(OC_4H_9)_3$，$Li(OC_4H_9)$のアルコキシドと水を溶解した塗布液から製膜し、１２０℃５分乾燥した後６００℃で焼結した。この塗布～焼結過程を繰り返してＬＩＳＩＣＯＮのイオン伝導層を１０μｍ製膜して電子伝導体とイオン伝導体の積層体を作製した〔図２（ａ）〕。次に得られた積層体の固体電解質側に金属リチウム（負極）を１０００Å蒸着し、さらに金属ホイルを圧着してリチウム電池を作製した〔図２（ｂ）〕。インピーダンスの周波数特性の測定による正極と固体電解質の界面抵抗は充放電を５０回繰り返してもほとんど変化がみられなかった。

実施例２

実施例１と同様にして表面に凹凸を有する二酸化マンガン焼結体を作製し、この上に電子伝導体とイオン伝導体の混合層を、二酸化マンガン粉末を分散した２－メトキシエタノール中に$Zr(OC_3H_7)_4$，$Si(OC_2H_5)_4$，$PO(OC_4H_9)_3$，$Li(OC_4H_9)$のアルコキシドと水を溶解した塗布液を用いて製膜し、１２０℃５分乾燥した後６００℃で焼結した。この塗布～焼結過程を繰り返して２０００Åの混合層を作製した。引き続き、この上に上記の塗布液から二酸化マンガンを除いた組成の溶液からＬＩＳＩＣＯＮのイオン伝導層を１０μｍ製膜して電子伝導体とイオン伝導体の積層体を作製した〔図３（ａ）〕。次に得られた積層体の固体電解質側に金属リチウム（負極）を１０００Å蒸着し、さらに金属ホイルを圧着してリチウム電池を作製した〔図３（ｂ）〕。インピーダンスの周波数特性の測定による正極と固体電解質の界面抵抗は充放電を５０回繰り返してもほとんど変化がみられなかった。

【０００６】

【効果】電子伝導体層とイオン伝導体層との界面が凹凸

状に接触していることにより、その界面の表面積を拡大させ、反応効率を向上させることができた。さらに前記両層の界面に、前記両伝導体の混合物質を設けることにより、電極反応における電子やイオンの移動が良好な積層体が得られた。

【図面の簡単な説明】

【図１】（ａ）は、凹凸を有する電子伝導層とイオン伝導層とよりなる積層体の断面図を示す。

（ｂ）は、イオン伝導層と凹凸を有する電子伝導層との界面に混合層を設けた積層体の断面図を示す。

【図２】（ａ）は、電子伝導層がMnO_2、イオン伝導層がＬＩＳＩＣＯＮで構成され、両層の界面が凹凸状である積層体の断面図を示す。

（ｂ）は、前記（ａ）のＬＩＳＩＣＯＮ層上に、蒸着Ｌ＊ｉ層およびＬｉホイルをそれぞれ設けた積層体の断面図を示す。

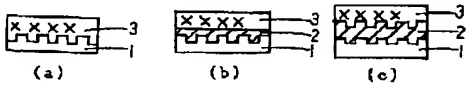
【図３】（ａ）は、ＬＩＳＩＣＯＮ層と凹凸を設けたMnO_2層の界面に、ＬＩＳＩＣＯＮとMnO_2よりなる積層体の断面図を示す。

（ｂ）は、前記（ａ）のＬＩＳＩＣＯＮ層上に、蒸着Ｌｉ層およびＬｉホイルをそれぞれ設けた積層体の断面図を示す。

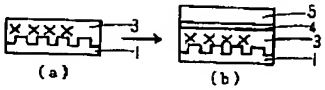
【符号の説明】

１　電子伝導層
２　混合層
３　イオン伝導層
４　蒸着Ｌｉ層
５　Ｌｉホイル

【図１】



【図２】



【図３】